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A STUDY OF THE GELATINIZING AGENTS, PASTY MATERIALS AND THICKENERS USED IN FOOD PRODUCTS.

By Leon A. Congdon.

THE use of gelatinizing agents, pasty materials and thickeners in food products has become quite prevalent in recent years. Hence a study of these materials and their detection in food products is important to the chemist. Quite often thickeners, pasty materials and gelatinizing agents are used to cheapen the genuine articles, in that they are used to represent the genuine articles. In this class might be mentioned agar-agar, which has been found in imitation lemon slices; starch, agar-agar and gelatine in imitation jelly; dextrin in imitation cocoa cubes; then again these materials are used to cover up inferiority. In this class might be mentioned albumen, or white of egg, which is sometimes used to glaze coffee beans to make them appear better than they really are. Again, the thickenings, etc., are used in such products as ice cream and custards, primarily to add bulk to the product, and to give the material in which they are used a frothy appearance. They are also used in this connection to make the ice cream and custards "stand up." A great many ice-cream manufacturers use a so-called "ice-cream powder." These "ice-cream powders" vary in composition, but generally contain one or combinations of the following: dextrin, acacia, tragacanth, gelatine, albumen, and starch.

This paper will deal more specifically with the detection of these gelatinizing agents, pasty materials, and thickeners. I will describe briefly the more common ones now in use.

Gelatine is usually regarded as an albuminoid, but does not come strictly within the requirements of the definition of simple proteins, which possess essentially the same chemical structure as the other proteins, but are characterized by great insolubility in all neutral solvents. Gelatine is prepared from bones and other animal parts, and is insoluble in cold water, but soluble in hot water. When the hot-water solution containing one per cent or more of gelatine cools it forms a jelly.

By prolonged boiling the gelatinizing power is lost. A solution of gelatine placed in the polariscope shows strongly lævorotary.

Starch belongs to the cellulose groups of carbohydrates. Carbohydrates are generally understood as being compounds of carbon, hydrogen, and oxygen, the last two elements being present in the proportion in which they occur in water. The cellulose groups ($C_6H_{10}O_5$) include starch, cellulose, dextrin, gums, etc. Pure starch is a glistening, white, granular powder having a peculiar feeling when rubbed between the thumb and finger. It is very hygroscopic, commercial starch containing about 18 per cent of moisture. Starch is very widely distributed in the vegetable kingdom, occurring in almost every plant at some stage in its growth. Starch is insoluble in cold water, alcohol, and ether; it is soluble in hot water, though not without a change. By boiling with dilute acids, starch is first converted by hydrolysis into a mixture of dextrin and maltose, and finally by prolonged boiling into dextrose. Malt extract also hydrolyzes starch in solution. Though the cereal and vegetable starches, whatever their origin, are identical chemically, the various starch granules have certain characteristics when viewed under the miscroscope that render their identification easy in most cases. The common starches used in commercial food products as pasty materials are wheat, corn, potato, rice, tapioca, buckwheat, barley, rye, etc.

Agar-agar is an important commercial gelatinizing agent. It has an entirely different composition than gelatine. "Agar-agar" is the East-Indian name for seaweed. It is soluble in hot water to a viscid, tasteless, odorless jelly. It is very similar to pectin, but usually considered as gelose (para-arabin—$C_6H_{10}O_5$). It is thus a carbohydrate. Agar-agar is known by various names, such as Japan agar; Japan, Bengal, Ceylon or Chinese isinglass. True agar-agar is an algæ, a species of seaweed. It is found principally in the Pacific and Indian oceans, and Japan sea.

Gum tragacanth, an important thickener, is used in such products as ice-cream powders. There are various uses for tragacanth in pharmacy. Gum tragacanth is the gummy exudation from *Astragulus gummifer.* Its habitat is Asia Minor, Syria, and Persia. The derivation of the word is from the Greek "tragos" (goat) and "akantha" (thorn, or horn); that is, the exuded gum acquires a horny consistency and appearance; or the plant is thorny and the edges of it resist the attack of goats. Gum tragacanth is usually found on the market in whitish ribbon-shaped bands, with thorny consistency, and translucent. With fifty parts of water it swells up and forms a cloudy, gelatinous mass. It is principally cellulose, soluble gum, and bassorin acid.

Dextrin is simply starch heated to 250° C. There are three different kinds of dextrin, which give different chemical color reactions than starch with iodine solution — amylodextrin, erythrodextrin, and achroödextrin. The dextrin principally found in commerce is amylodextrin. Dextrin may also be made from starch by heating starch with dilute mineral acids, or diastase. It is a whitish powder, soluble in water. Dextrin has been known to be used as a constituent of certain ice-cream powders. It is sometimes substituted for acacia.

Gum arabic or acacia is the gummy exudation from *Acacia senegal.* Its habitat is East and West Africa, Arabia, Senegal, Kordofan, Egypt, India, and Nubia. The name comes from the Greek "akakia," a thorny Egyptian tree, and "ake," meaning a point. It is soluble in two parts water, but insoluble in alcohol. Its principal chemical constituents are arabin (arabic acid; gummic acid—$C_{12}H_{22}O_{11}$, or $C_{10}H_{18}O_2$) and para-arabin, usually in the form of calcium, magnesium and potassium arabates.

Albumen. There are two commercial kinds of albumen—the egg albumen, from white of eggs; and the blood albumen, from blood serum. Both are soluble in about eight parts of water. Albumen is a nitrogenous compound, and comes in the classification of the single proteins soluble in water and coagulable by heat. For the purpose of this paper, it is not necessary to go into the classification of the proteins.

Fruit or vegetable pectins. Very little is known about the pectin bodies of fruits and vegetables, but pectin is supposed to be a carbohydrate, similar in its properties to starch. Bracennont, who first investigated pectin, pointed out that he could obtain a gelatinizing agent from alkaline pectates which he isolated from carrots by treating the latter with alkalies. He accomplished this in 1825, and made jellies by dissolving these alkaline pectates in water, heating with sugar and then adding a small quantity of mineral acid. In 1909 and 1910, Goldwaite, by the methods of Chodnew and of

Fremy, obtained pectin from crabapple, grape, sweet-apple and peach juices, and from the white inner skins of oranges and lemons. The uncooked juices of apple, quince, lemon and orange, according to Goldwaite, did not contain pectin, but the uncooked fruit juices of currants and blackberries did contain pectin. It has long been known that the cooked fruit juices of apples, quinces, currants, blackberries, crabapples, grapes, plums, raspberries, peaches, barberries, cranberries, blueberries, pears, and, with care, cherries and stawberries, contain a substance which will form a jelly. Where the process of jelly making originated is not definitely known. The pectin, or the jellying principle, is still unsolved, but Bigelow, Parloa, Goldwaite and Leach have stated that in their opinion pectin is supposed to be a carbohydrate, similar in its properties to starch, while Herzfield regarded the pectin bodies as combinations of araban and galactan, and Tollens has suggested that they may be glucosides. All investigators have agreed, however, that the pectin is the gelatinizing agent. The principal theory is that pectose and pectase always exist in the unripe fruit, and when the fruit ripens the pectase acts upon the pectose, which is insoluble in water, converting it into pectin, which is soluble. Pectin is at its best when the fruit is just ripe or a little before. The French chemist Mangin divides the pectose groups into two series: (1) Neutral bodies which vary in their solubility in water. At one extreme we have the substance pectose, which is insoluble in water and closely associated with cellulose; at the other extreme the substance known as pectin, which is soluble in water but tends to form a jelly fairly readily. Intermediately between these are bodies of a gelatinous nature. (2) Substances allied to this group are feeble acids, the chief member of which occurs as calcium pectate; the latter forms a binding substance between the pores of many plants.

Decomposition of pectose bodies. Wienogradski and his pupils say it is due to anaërobic bacillus which will decompose pectin and calcium pectate, but has no action on cellulose. Flax is held together by an integument consisting of calcium pectate. This is gotten rid of by a fermentation process which decomposes the integument while leaving the fiber intact.

This important enzyme—pectose—which gelatinizes fruit juice containing pectin, plays an important part with calcium salts, so it seems, and I am of the opinion that it throws some light on the jellying principle of fruit jellies. For instance, investigators have proved that fruit juices containing acid and pectin can be made into a jelly by heating, then adding sugar and heating again; likewise, fruit juices having considerable pectin and but little acid fail to jell, but if acid is added the substance forms a jelly. My theory is that when the acid is added to the calcium pectate, the calcium forms the salt of the added acid and frees the pectic acid; the pectic acid pectase clots the mass, and on cooling forms the jelly. When the fruit juice contains sufficient amount of acid in itself and no added acid is necessary, the action of the calcium pectate is with the fruit acid, etc. That pectin can be hydrolyzed by acids present if boiled sufficiently long has been proven by Goldwaite.

The following table, prepared and worked out by the writer on actual experiments in the laboratory, places the above-mentioned materials in six groups: Group I, the iodine solution group; Group II, the acid nitrate of mercury group; Group III, the concentrated solution of sodium borate group; Group IV, the solution of sodium hydrate group; Group V, the solution of mercuric chloride group, and Group VI, the solution of cuprammonia group.

A careful study of this group method shows that a new method for testing agar-agar has been discovered. This test is based on Groups II, III and IV, and the characteristic reactions for agar-agar depends on a new test for acacia in Group II, which is: the test with one drop of acid nitrate of mercury plus the unknown water solution yields a stringy gelatinous precipitate, *soluble in excess of the reagent.* Since the next group reagent, the concentrated solution of sodium borate, in Group III, only precipitates agar-agar and acacia, it is simply a test to prove whether one or both are present in the unknown water-soluble mixture. Going to Group IV, the solution of sodium hydrate group, this group reagent does not precipitate agar-agar, and hence if no precipitate is obtained agar-agar is absent, although if a white cloudy precipitate occurs the unknown is acacia, and if a brownish-yellow color occurs on heating the unknown is tragacanth. Acacia may be further tested for with a solution of soluble basic lead acetate, which gives a white gelatinous precipitate; and again tested for by the acid nitrate of mercury test in Group II, as already indicated. The remaining tests in the other groups given in the table are rather well known, but the writer thinks that this group method will be helpful to those interested in food chemistry.

Group Reactions.

Groups.	*Group reagents.*	*Reactions with water-soluble solutions of the gelatinizing agents, pasty materials and thickeners.*
Group I.	Iodine solution.	Blue coloration indicates *starch*. (Sometimes green apples made into jelly will give traces of starch.)
		Purple coloration indicates *amylodextrin*.
		Red coloration indicates *erythrodextrin*.
		No coloration may indicate neither starch nor dextrin, but may be *achroödextrin*.
Group II.	Millon's or Stoke's reagent (acid nitrate of mercury).	Filtrate, after shaking substance in solution with reagent, is not clear, but cloudy. Filtrate picric acid solution—yellow precipitate indicates *gelatine*.
		Solution plus drop of this reagent yields a gelatinous precipitate, soluble in excess of this reagent, which indicates *acacia*.
		A slight white cloudy precipitate may indicate either *agar-agar* or *tragacanth* or both (test for *tragacanth* as in Group IV).
Group III.	Concentrated solution of sodium borate.	Yields a white gelatinous precipitate, which indicates either *agar-agar* or *acacia* or both.
		C. T. *Acacia* will give a gelatinous, opaque white precipitate with solution basic lead acetate.
		Acacia may be further tested for as in Group II or Group IV, or by adding a solution of tannin, which gives a bluish-black coloration.
Group IV.	Solution of sodium hydrate.	Yields brownish yellow color on heating, which indicates *tragacanth*.
		Yields a white cloudy precipitate, indicates *acacia*.
Group V.	Solution of mercuric chloride.	A slight turbidity may indicate *dextrin*.
		A white precipitate may indicate *albumen* and *gelatine*.
Group VI.	Schweitzer's reagent (solution of cuprammonia).	If a concentrated water solution of the unknown is treated with this reagent and placed on glass slide under microscope, a delicate framework of cupric pectate is evident, showing a *pectin* of fruit or vegetable origin present.